Circular Dichroism in Photoelectron Angular Distributions from Oriented Linear Molecules

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We show that circular dichroism exists in the photoelectron angular distributions from oriented linear molecules in the electric dipole approximation. Contributions to the dichroism arise solely from interferences between degenerate photoelectron continua with m values differing by ± 1. We identify specific photon-propagation, electron-detection configurations where circular dichroism will be observable. Finally, we illustrate the magnitude of this effect through *ab initio* calculations for photoionization out of the 4σ orbital of an oriented CO molecule.

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Circular dichroism (CD) is a phenomenon in which the responses of a system to left and right circularly polarized light are different. Traditionally, CD has been observed in solutions of chiral molecules through the rotation of the plane of polarization of linearly polarized light (optical rotary dispersion), or through the conversion of linearly polarized light to elliptically polarized light.[1] Several recent theoretical analyses[2-7] have predicted CD in photoelectron angular distributions (CDAD). These studies either assumed a chiral molecule, included spin-orbit interaction, or went beyond the electric dipole approximation. In this Letter we demonstrate CDAD from *oriented linear molecules within the electric dipole approximation.* This CDAD appears in the absence of any spin-orbit interaction. We show that only interference terms between degenerate photoelectron continua with the m values differing by ± 1 contribute to CDAD. This feature gives better resolved information than is available from linear-polarization studies and hence can be a useful tool in the study of oriented molecules. We also identify the photon-propagation and electron-detection geometrics in which CDAD can be observed. Finally, we illustrate the magnitude of this effect by calculating the CDAD in the photoionization of the 4σ orbital of CO oriented normal to a surface. In a recent paper focusing on CD from chiral molecules, Cherepkov[7] alluded to the existence of CDAD in linear molecules. In our paper, we carry out the analysis in greater detail stressing the importance of this phenomenon.

The doubly differential photoionization cross section, in the molecular frame, is defined as[8]

$$\partial^2\sigma/\partial\Omega_{\hat{\mathbf{k}}}\partial\Omega_{\hat{\mathbf{n}}} = (4\pi^2 E/c)\,|I_{\mathbf{k},\hat{\mathbf{n}}}|^2, \tag{1}$$

where E denotes the photon energy and $I_{\mathbf{k},\hat{\mathbf{n}}}$ the bound-continuum matrix element[8]

$$I_{\mathbf{k},\hat{\mathbf{n}}} = k^{1/2}\langle\psi_i|\mathbf{r}\cdot\boldsymbol{\epsilon}|\psi_{f,\mathbf{k}}^{(-)}\rangle. \tag{2}$$

For convenience, we discuss the one-electron case and consider ionization out of an initial orbital ψ_i into a continuum orbital $\psi_{f,\mathbf{k}}^{(-)}$. In this equation, $\mathbf{k}$ is the photoelectron momentum and $\boldsymbol{\epsilon}$ is the unit polarization vector of the photon. The unit vector $\hat{\mathbf{n}}$ corresponds to the direction of polarization for linearly polarized light and to the direction of propagation for circularly polarized light. Assuming a partial-wave expansion for $\psi_{f,\mathbf{k}}^{(-)}$, we can write $I_{\mathbf{k},\hat{\mathbf{n}}}$ as

$$I_{\mathbf{k},\hat{\mathbf{n}}} \equiv I_{\mathbf{k},\hat{\mathbf{n}}}^{\mu_0} = \sum_{lm\mu} I_{lm\mu} Y_{lm}^*(\Omega_{\hat{\mathbf{k}}}) D_{\mu,\mu_0}^{1}(\Omega_{\hat{\mathbf{n}}}), \tag{3}$$

where the polarization index μ_0 is zero for linearly polarized light and ± 1 for circularly polarized light. The rotation matrices $D_{mm'}^{l}$ are defined in the convention of Rose.[9] The dynamical coefficients $I_{lm\mu}$ are defined as

$$I_{lm\mu} = k^{1/2}\langle\psi_i|r_\mu|\psi_{fklm}\rangle \tag{4a}$$

with

$$r_\mu = \begin{cases} \mp(x \pm iy)/2^{1/2} & \text{for } \mu = \pm 1, \\ z & \text{for } \mu = 0. \end{cases} \tag{4b}$$

In principle, the summation over l in Eq. (3) extends to infinity. However, in practice, this summation can be cut off at some $l = l_{\max}$ as very high partial waves contribute insignificantly to $I_{\mathbf{k},\hat{\mathbf{n}}}^{\mu_0}$.

The CDAD signal is defined as the difference in the differential cross sections of Eq. (1) for left and right circularly polarized light. This quantity is proportional to the difference

$$|I_{\mathbf{k},\hat{\mathbf{n}}}|_{L-R}^2 = |I_{\mathbf{k},\hat{\mathbf{n}}}^{+1}|^2 - |I_{\mathbf{k},\hat{\mathbf{n}}}^{-1}|^2. \tag{5}$$

Upon squaring of Eq. (3) and combining of spherical harmonics and rotation matrices, this difference can be

written as

$$|I_{\mathbf{k},\hat{\mathbf{n}}}|^2_{L-R} = \frac{1}{\sqrt{3}}\langle 1\,1,-1\,1|1\,0\rangle \sum_{L=0}^{2l_{\max}} \sum_{M=-1}^{1} (2L+1)^{-1/2} \times \sum_{\substack{lm\mu \\ l'm'\mu'}} (-1)^{m+\mu}[(2l+1)(2l'+1)]^{1/2}[I_{lm\mu}I^*_{l'm'\mu'} - I^*_{l,-m,-\mu}I_{l',-m',-\mu'}] \times \langle ll'00|L\,0\rangle \langle ll',-mm'|LM\rangle \langle 1\,1,-\mu\mu'|1,-M\rangle Y_{LM}(\theta_k,\phi_k) Y_{1,-M}(\theta_p,\phi_p). \quad (6)$$

In the above equation, $M = m' - m = \mu - \mu'$ and, (θ_k, ϕ_k) and (θ_p, ϕ_p) denote respectively the spherical polar angles in the molecular frame for the electron and photon propagation directions. The molecular frame is defined with the z axis coinciding with the internuclear axis. Note that when we combine the rotation matrices $D^1_{\mu\mu_0} D^{1*}_{\mu'\mu_0}$ into $D^{L'}_{M0}$, only $L' = 1$ terms survive in Eq. (6) because of the symmetry of the Clebsch-Gordan coefficients.

For linear molecules, $I_{lm\mu} = I_{l,-m,-\mu}$ and hence the $M = 0$ term vanishes in Eq. (6) and the $M = \pm 1$ and -1 terms become equal. $|I_{\mathbf{k},\hat{\mathbf{n}}}|^2_{L-R}$ then simplifies to

$$|I_{\mathbf{k},\hat{\mathbf{n}}}|^2_{L-R} = \frac{4}{\sqrt{3}}\langle 1\,1,-1\,1|1\,0\rangle \sum_{L=0}^{2l_{\max}} (2L+1)^{-1/2} \sum_{\substack{lm\mu \\ l'm'\mu'}} (-1)^{m+\mu}[(2l+1)(2l'+1)]^{1/2}\langle ll'00|L\,0\rangle \times \langle ll',-mm'|L,-1\rangle \langle 1\,1,-\mu\mu'|1\,1\rangle \mathrm{Im}[I_{lm\mu}I^*_{l'm'\mu'}]\,\mathrm{Im}[Y_{L,-1}(\theta_k,\phi_k) Y_{11}(\theta_p,\phi_p)]. \quad (7)$$

This equation, combined with Eqs. (1) and (5), describes the CDAD from oriented linear molecules.

Several general features of CDAD follow from Eq. (7). These include the following:

(i) CDAD is due only to interference terms between degenerate photoelectron continua differing by ± 1 in their m values ($m' - m = \pm 1$). For example, in photoionization from a σ orbital, CDAD will be due solely to the interference between the $k\sigma$ and $k\pi$ continua. This follows from the Clebsch-Gordan coefficient $\langle ll', -mm'|L, -1\rangle$ and the interchangeability of m and m'.

(ii) CDAD vanishes if $\hat{\mathbf{k}}$, $\hat{\mathbf{n}}$ and the molecular axis are coplanar. This result arises because $\mathrm{Im}[Y_{L,-1}(\theta_k,\phi_k) Y_{11}(\theta_p,\phi_p)]$ is proportional to $\sin(\phi_p - \phi_k)$ and, if $\phi_p - \phi_k = n\pi$ ($n = 0, \pm 1$), $\sin(\phi_p - \phi_k) = 0$. A physical interpretation of this second feature, the main criterion for observing CD, can be seen as follows. Let $\hat{R}$ and $\hat{L}$ denote respectively the interaction operator $\mathbf{r}\cdot\boldsymbol{\epsilon}$ for right and left circularly polarized light propagating in a given direction. These operators are related to each other by a reflection in a plane containing the propagation direction. If $\hat{P}$ denotes this reflection operator, we have

$$\hat{R} = \hat{P}\hat{L}\hat{P}^{-1} = \hat{P}\hat{L}\hat{P}. \quad (8)$$

Then

$$|I_{\mathbf{k},\hat{\mathbf{n}}}|^2_L = k\,|\langle\psi_i|\hat{L}\,|\psi^{(-)}_{f\mathbf{k}}\rangle|^2 \quad (9a)$$

while

$$|I_{\mathbf{k},\hat{\mathbf{n}}}|^2_R = k\,|\langle\psi_i|\hat{R}\,|\psi^{(-)}_{f\mathbf{k}}\rangle|^2 = k\,|\langle\psi_i|\hat{P}\hat{L}\hat{P}|\psi^{(-)}_{f\mathbf{k}}\rangle|^2. \quad (9b)$$

Since the reflection plane can always be chosen to contain the molecular axis, $|\psi_i\rangle$ will always have definite parity with respect to $\hat{P}$. If $\mathbf{k}$ lies in this plane, then $|\psi^{(-)}_{f\mathbf{k}}\rangle$ will also have a definite parity under $\hat{P}$. In this case, $|I_{\mathbf{k},\hat{\mathbf{n}}}|^2_L = |I_{\mathbf{k},\hat{\mathbf{n}}}|^2_R$ and CDAD vanishes. For linear molecules adsorbed normal to a surface, this conclusion implies that CDAD will not exist in the plane of incidence.

(iii) For linear molecules with an inversion center (homonuclear diatomics, for example), CDAD does not exist in the reflection plane perpendicular to the molecular axis. This result follows from the fact that for molecules with an inversion center, l, l' are either even (g states) or odd (u states). In this case, the Clebsch-Gordan coefficient $\langle ll'00|L\,0\rangle$ insures that L is even. Because $\theta_k = \pi/2$ for the reflection plane perpendicular to the molecular axis, CDAD vanishes in this plane as $Y_{L,-1}(\pi/2, \phi_k) = 0$ for L even.

Molecules adsorbed on surfaces are good candidates for demonstrating CDAD. For example, CO is known to be adsorbed perpendicular to the Ni(100) surface with the carbon end pointing towards the surface.[10] In Fig. 1(a), we present the results of our calculation of CDAD resulting from photoionization of the 4σ orbital for an isolated CO molecule oriented normal to a surface. Such a system can be a useful model for photoemission from actual adsorbed molecules.[11] We examine the case in which the photon approaches the surface at 45° with the normal [$(\theta_p, \phi_p) = 135°, 0°$)] and the electrons are collected in a plane perpendicular to the plane of incidence ($\phi_k = 90°$). The continuum wave functions were obtained by the Schwinger varia-

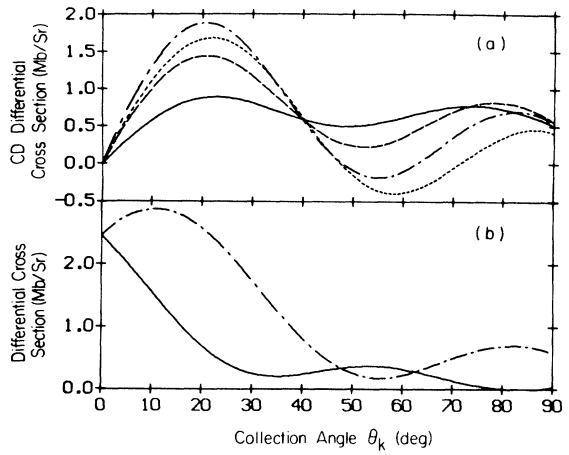

FIG. 1. (a) CD differential cross section vs the collection angle θ_k. Different curves correspond to photon energies $E = 30.7$ eV (solid line), 33.3 eV (long-dashed line), 36.2 eV (dot-dashed line), and 40.8 eV (short-dashed line). Photon propagation direction is $(\theta_p, \phi_p) = (135°, 0°)$ and electron collection is in the plane $\phi_k = 90°$. (b) Differential cross sections for left (dot-dashed line) and right (solid line) circularly polarized light at $E = 36.2$ eV. Configuration of angles is as in (a).

tional method.[8,12] The results are plotted as a function of θ_k for various photon energies E. The energy range chosen scans the well-known shape resonance in the $4\sigma \rightarrow k\sigma$ channel.[13] In Fig. 1(b) we have also plotted, for comparison, the differential cross sections for right and left circularly polarized light at $E = 36.2$ eV.

The most striking aspect of Fig. 1 is that CDAD is of the same order of magnitude as the differential cross section itself. Notice the "magic angle" at $\theta_k \approx 40°$ at which all the distributions have the same magnitude. The behavior of CDAD at this angle can be understood as follows. The resonance feature in the 4σ ionization is known to be in the $l = 3$ wave of the $k\sigma$ continuum.[13] Thus, only I_{300} is rapidly varying with energy around the shape resonance and the CDAD's assume the character

$$Y_{30}(\theta_k, \phi_k) \sum_{l'} I_{l'1,-1} Y^*_{l'1}(\theta_k, \phi_k).$$

The magic angle at $\theta_k \approx 40°$ is due to the zero of $Y_{30}(\theta_k, \phi_k)$ at $\theta_k = 39.2°$. Similarly, at $\theta_k = \pi/2$, the convergence of CDAD's is again due to the vanishing of $Y_{30}(\theta_k, \phi_k)$. CDAD itself is nonvanishing at these angles because of the contributions of $l \neq 3$ partial waves in the $k\sigma$ channel. Figure 1(a) clearly displays how CDAD highlights the particular partial wave and the partial channel in which the resonances is located. In conclusion, we have shown that CDAD exists for oriented linear molecules within the electric dipole approximation and is of the same magnitude as the differential cross section. We have identified configurations of molecular orientation and photon-propagation and electron-detection directions in which CDAD will be seen. More importantly, we have shown that CDAD arises as a result only of interferences between degenerate continuum channels with $\Delta m = \pm 1$. For this reason, we believe CDAD studies can be useful in extracting information which can be more difficult to obtain from linear polarization studies. It should also be possible to use CDAD to study the characteristics of adsorbed molecules.

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